



NRL/MR/6795--00-8481

Practical Issues in Applying Ultra-Broadband (UB) Radiation to the Monitoring of Hazardous Air Pollutants (HAPs) at Extended Distances

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November 27, 2000

20001213 141

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE November 27, 2000	3. REPORT TYPE AND DATES COVERED Interim	
4. TITLE AND SUBTITLE Practical Issues in Applying Ultra-Broadband (UB) Radiation to the Monitoring of Hazardous Air Pollutants (HAPs) at Extended Distances			5. FUNDING NUMBERS
6. AUTHOR(S) A. Ting, J. Qiu,* and C. Manka**			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Washington, DC 20375-5320			8. PERFORMING ORGANIZATION REPORT NUMBER NRL/MR/6795--00-8481
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5660			10. SPONSORING/MONITORING AGENCY REPORT NUMBER SERDP Program Office 901 North Stuart Street, Suite 303 Arlington, VA 22203
11. SUPPLEMENTARY NOTES *NRC/NRL Post-Doc **RSI, Inc., Lanham, MD 20706			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) The ultra-broadband (UB) radiation source that is being developed at the Naval Research Laboratory (NRL) has the potential to become a versatile source of radiation for active remote sensing of chemical hazardous air pollutants (HAPs) at extended distances. However, before the realization of this important application of the radiation source, some of the practical issues involved in the research and development of the technique of UB generation and HAP detection have to be looked at. These issues include the list of possible candidate HAPs for the present wavelength range of the UB radiation and the various background noise level and the related signal-to-noise ratios. This report will provide a semiquantitative analysis of these issues and provide discussions on some of the complexities that still need to be resolved.			
14. SUBJECT TERMS Ultra-broadband radiation Remote sensing Signal-to-noise ratio			15. NUMBER OF PAGES 13
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

I. Introduction

The application of UB radiation to HAP detection is an extension of Lidar (light detection, and ranging [ref 1]) and its cousin Dial (differential absorption lidar [ref 1]). In both of these schemes, laser beams with one frequency (Lidar) or two frequencies (Dial) are projected at a distance to the target region containing the HAPs and the return signals are monitored and analyzed. A particular HAP has to be known ahead of time so that the proper frequency(ies) can be chosen for the laser(s). Most lasers still operate at discrete frequencies that may not match the peaks of the scattering frequencies of many HAPs. In addition, different HAPs usually require physically different lasers. Therefore, an UB radiation source with laser-like propagation properties can allow detection of more than one (multiple) HAP since a wide and continuous spectrum of frequencies is available.

Some of the capabilities of UB radiation active remote sensing can be examined using the known analyses developed for Lidar and Dial by examining one frequency (HAP) at a time out of the broad spectrum. However, such analyses only show the capabilities of this new technique from the traditional point of view of Lidar and Dial. The continued development of algorithms that can handle analyses of the whole UB active remote sensing spectrum will lead to more accurate HAP measurements than using the traditional analysis techniques. It is in this spirit that the following sections will attempt to analyze, in the framework of Lidar and Dial, the UB active remote sensing and provide projections, using presently known data, of how far this technique may go.

II. HAPs suitable for UB active remote sensing

The UB active remote sensing technique relies on the absorption of the UB radiation by the HAP. Therefore, in principle, the HAPs that can be detected depend only on their absorption characteristics. Most HAPs are chemical molecules which have molecular absorption bands of vibration and rotation ranging from the near- infrared of 1-3 μm for very small molecules to the mid- and far-infrared of $> 10 \mu\text{m}$ for larger and more complex molecules. However, in practice, only those that have their absorption

structures inside the spectra of available radiation sources could be detected. For example, in passive remote sensing where sunlight is used as the radiation source, the very broad spectral content of sunlight allows the detection of most HAPs. However, in active remote sensing such as Lidar and Dial, until recently the available laser wavelengths have been either in the visible and near-UV or the far-infrared near the CO₂ lasers. The lack of appropriate lasers with suitable wavelengths has made a lot of molecules with absorption structures not coinciding with the laser wavelengths inaccessible for detection by these methods. We have generated UB radiation with wavelengths ranging continuously from 0.527 μm to 2.2 μm . Therefore, any chemical molecules with absorption structures in this broad range may now be detected when this UB radiation is used for active remote sensing.

Since the presently available UB radiation has a wavelength range of <2.2 μm , one would expect only the smaller diatomic molecules to be the ones that can be detected. However, some larger and more complex molecules have overtones and combination bands of their fundamental absorption lines (higher order and therefore more energetic transitions) that are of higher frequencies (shorter wavelengths) and lie within the presently available wavelength range. Some of these bands were charted only recently with the advance of tunable diode lasers [ref 2,6].

A quick run of the atmospheric radiation transmission code HITRAN in the wavelength range of 1-2 μm shows the following gases to have absorption lines there. They are carbon dioxide (CO₂), nitrous oxide (N₂O), carbon monoxide (CO), methane (CH₄), hydroxyl radical (OH), ammonia (NH₃), hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen iodide (HI). Recent literatures have also listed absorption lines in the <2 μm range for nitric oxide (NO) [ref 3,4], nitrogen dioxide (NO₂) [ref 3,5], acetylene (C₂H₂) and hydrogen cyanide (HCN) [ref 2].

The list of chemicals that can be detected by the UB radiation active remote sensing will become longer as, a) more chemicals are charted for their overtone absorption bands in the wavelength range of 1-2 μm , and b) the UB radiation spectrum extends into longer wavelengths when the method of generation improves.

III. Sample gas detection using UB radiation and signal/noise calculations

As described in the introduction, because of the novel features of the UB radiation, it is inherently complex to make precise estimates of the concentration of chemicals that the UB active remote sensing can detect. As the source characteristics are known better and the analysis tools are developed further with our present research efforts, we will have more refined calculations most probably through elaborate computer analysis programs. To illustrate the possible power of the UB active remote sensing method, we will study a sample gas chemical in the framework of multi-wavelength Dial.

We shall assume the UB source and the detector are on the same side of the HAP source. This way, we do not have to place a retro-reflecting mirror on the other side of the HAP source or have to rely on some topographical feature to provide the reflected UB signal. The incoming UB radiation is derived from scattering of the outgoing UB radiation by scattering particles in the HAP source. This is commonly known as the differential absorption and scattering (DAS) technique.[ref 1] We will begin with the Lidar scattering equation for received energy $W_r(\lambda)$ and transmitted energy W_t [ref 1], which is

$$W_r(\lambda) = W_t K T(R) \frac{A}{4\pi R^2} N(R) \sigma_s(\lambda) \frac{c \tau_d}{2} \frac{\Delta\lambda}{\lambda}, \quad \text{Eq. (1)}$$

where K is the geometric detector efficiency, $T(R)$ is the atmospheric transmission efficiency, A/R^2 is the acceptance solid angle of the detector, $N(R)$ is the density of the scattering particles, $\sigma_s(\lambda)$ is the total scattering cross section of the particles, τ_d is the detector gating time, and $\Delta\lambda/\lambda$ is the resolution bandwidth. The application of this single frequency Lidar equation to the UB radiation is through $\Delta\lambda/\lambda$ which defines the selected outgoing radiation wavelength from the UB spectrum. This equation provides the return signal from a scattering source such as a smoke stack where $\sigma_s(\lambda)/4\pi$ is the differential scattering cross section for back scattering.

We shall now consider two major sources of elastic scattering processes in air, namely Rayleigh scattering and Mie scattering, where the wavelengths of the radiation are not changed after scattering. Rayleigh scattering is the elastic scattering of radiation from atoms and molecules while Mie scattering is the elastic scattering from small particulates. We shall assume a nominal wavelength of $1 \mu\text{m}$ in our analysis for our UB

radiation. At this wavelength, the Rayleigh scattering cross section is about 10^{-27} cm^2 [ref 7], while the Mie scattering cross section of, for example, 0.1 μm water droplets is $\sim 3 \times 10^{-12} \text{ cm}^2$ [ref 1]. Therefore, in considering the amount of back scattered radiation that reaches the detector, the Mie scattering process far outweighs the Rayleigh scattering.

We can estimate the concentration of particulates that will be required to provide enough back scattered radiation by using the Beer-Lambert law, $I(L) = I(0)\exp(-N\sigma_s L)$, where $I(L)$ is the radiation intensity after passing through distance L in a medium with concentration N of a scatterer or absorber with cross section σ_s . For a 90% Mie scattering of the incoming radiation in a 30 m thick scattering column, i.e., $L = 3 \times 10^3 \text{ cm}$, the particulate concentration is 1×10^{11} (10 parts per trillion) using the Mie scattering cross section above.

Similarly, the loss of radiation due to Rayleigh scattering after the radiation has passed through 1 km ($L=10^5 \text{ cm}$) of clear atmosphere is only 0.26%. We can therefore assume $T(R) \sim 1$ in Eq. (1) for transmission of the radiation up to the Mie scattering region. However, the attenuation of the radiation within the scattering region both as it is entering and leaving after reflection needs to be accounted for. This can be estimated by applying the Beer-Lambert law twice to obtain $T(L) = \exp(-2N\sigma_s L)$.

To estimate the number of photons back-scattered from the HAP source, we may assume a detector area of 1 m^2 aiming at a HAP source 1 km away, $K \sim 1$ for perfect alignment of the detector with the UB illuminated area of the HAP source, a detector gating time of 30 nsec ($c\tau_d = 10 \text{ m}$, $L = 5 \text{ m}$), resolution bandwidth of $\Delta\lambda/\lambda = 10^{-3}$ (1 nm at 1 μm , about 1 pixel in our spectrometer/detector setup), and Mie scattering cross section and particulate density as described above. These parameters lead to a ratio of $W_r/W_t = 2.8 \times 10^{11}$. The attenuation of the radiation through the HAP gives $T(L) = 0.46$. For a UB radiation source that has an average power of 1 watt at a repetition rate of 1 kHz, the energy per pulse $W_t = 1 \text{ mJ}$ which is 5×10^{15} photons around 1 μm wavelength. (Our present UB radiation source is generating approximately the same amount of energy per pulse but at a slower repetition rate.) The number of photons received by the detector from the Mie scattering in the HAP within the wavelength resolution bandwidth is

therefore 6.4×10^4 . Using an Indium Gallium Arsenide (InGaAs) detector which has a responsivity of 1 A/W and a read noise of 200 electrons, [ref 8] the signal to electronic noise ratio is ~ 320 .

Another primary noise source for the detector, especially during daytime operation, is the background sunlight. The diffuse component of typical background sky spectral radiance from sea level at zenith angle of 45 degrees is $\sim 10^{-4} \text{ Wcm}^{-2}\text{sr}^{-1}\mu\text{m}^{-1}$ near $1 \mu\text{m}$ [ref 7]. For a detector area of 1 m^2 , range of 1 km, a bandwidth of $0.001 \mu\text{m}$, and a detector gate time of 30 nsec, the noise level is 150 photons or a S/N ratio of 400. Considering both of these two sources of noise, the signal to noise level for the detector system is therefore >300 .

To study the absorption spectra of UB radiation by the HAPs in the framework of Lidar and Dial, we use the Lidar equation where the transmission coefficient $T(R)$ in Eq. (1) is explicitly written out,

$$P_r(\lambda) = P_t K \rho \frac{A}{\pi R^2} \exp[-2(\sigma(\lambda)N + \alpha(\lambda)L)] \quad \text{Eq. (2)}$$

where P_t and P_r are the transmitted and received power, ρ is the reflection efficiency which contains most of the terms that are listed in Eq. (1), $\sigma(\lambda)$ is the absorption cross section of the HAP whose concentration is given by N , and $\alpha(\lambda)$ is the extinction coefficient of the atmosphere due to various scattering processes other than the absorption in consideration. The exponential factor is just the Beer-Lambert law of the transmission of radiation at wavelength λ through the thickness L of the HAP column where we have assumed the radiation suffered no attenuation in distance R before reaching the HAP column.

When a two frequency Dial is used, Eq. (2) is repeated for the two wavelengths, λ_0 and λ_1 , which are respectively the wavelength at the center and the wing of the absorption structure of the HAP. By taking the ratio of the corresponding two equations and inverting the exponentiation, we can obtain an estimation of the concentration N as

$$N = \frac{1}{2(\sigma(\lambda_0) - \sigma(\lambda_1))L} \left[\ln\left(\frac{P_r(\lambda_1)}{P_r(\lambda_0)}\right) + B(\lambda_0, \lambda_1) \right]. \quad \text{Eq. (3)}$$

The term $B(\lambda_0, \lambda_1) = \ln(\rho(\lambda_0)/\rho(\lambda_1)) - 2L(\alpha(\lambda_0) - \alpha(\lambda_1))$ represents the effect of the background caused by the scattering ρ and attenuation α which need to be known *a priori* before the concentration N can be obtained. For narrow absorption structures in the spectrum of a HAP, the wavelength dependence of ρ and α may be assumed to be unchanged between λ_0 and λ_1 . In such case, B may be assumed to be zero. However, for most molecules, the absorption structures are vibrational and rotational bands that are quite broad. The constancy of ρ and α across the absorption band should therefore be questioned.

If one can extend the Dial to include a third wavelength, λ_2 , located at equal yet opposite distance from λ_0 as it was for λ_1 , and that the dependence of ρ and α with λ is linear, then one can show easily that the background term B is eliminated. If, in addition, the absorption cross section $\sigma(\lambda_1)$ and $\sigma(\lambda_2)$ are the same on both sides of the absorption band, then Eq. (3) can be simplified to

$$N = \frac{\ln(\sqrt{P_r(\lambda_1)P_r(\lambda_2)}/P_r(\lambda_0))}{2L(\sigma(\lambda_0) - \sigma(\lambda_{1,2}))}. \quad \text{Eq. (4)}$$

This treatment is natural for the UB radiation active remote sensing since the UB radiation has all the wavelengths available for selecting λ_1 and λ_2 for any λ_0 .

As an example, we shall assume an absorption signal strength of $P_r(\lambda_{1,2})/P_r(\lambda_0) = 1.0033$ which is within the S/N ratio we established above. This is equivalent to an absorption signal to noise ratio $S_a/N = 1$. If we also assume that $\sigma(\lambda_{1,2}) \sim 0$, the concentration of a HAP in an $L = 5$ m air column is then related to its absorption cross section by Eq. (4) to be

$$N [\text{cm}^{-3}] \sigma(\lambda_0) [\text{cm}^2] \sim 3.3 \times 10^{-6} [\text{cm}^{-1}]. \quad \text{Eq. (5)}$$

This formula provides a very simple estimation of the concentration once we know the absorption cross section of a HAP. The following is a table of few examples of HAP concentrations that may be detected based on Eq. (5).

Table I

HAP	Wavelength (μm)	Cross section (cm^2)	Concentration (ppm)
NO	1.795	7.0×10^{-23} [ref 4]	1700

N ₂ O	1.523	3.0x10 ⁻²³ [ref 4]	4100
CO	1.564	1.7x10 ⁻²³ [ref 4]	7200
	4.609	4.6x10 ⁻²⁰ [ref 5]	2
CO ₂	1.572	2.2x10 ⁻²³ [ref 4]	5500
CH ₄	1.645	6.5x10 ⁻²¹ [ref 9]	20
C ₂ H ₂	1.52	1x10 ⁻²⁰ [ref 10]	12
HCl	1.738	6x10 ⁻²⁰ [ref 11]	2
NH ₃	1.974	1x10 ⁻¹⁹ [ref 11]	1

The cross sections listed in the table have been normalized to the 1 nm bandwidth of the detector system.

IV. Discussions and future research and development goals

The above analysis is quite general and practical in the sense that actual parameters and components are used. It is still only a partial look at the real UB remote sensing technique because the UB radiation provides many more wavelengths than a mere three-wavelength Dial analysis can utilize. The fact that a three-wavelength Dial analysis can eliminate a linear background indicates that a multi-wavelength Dial analysis can model a much more complicated background contribution to the return signal. Conceptually, with the UB radiation, one can perform multi-wavelength Dial analysis on multi-HAPs. At this time, we are developing a signal processing technique (Kalman filtering) to analyze the entire spectrum simultaneously for multiple HAPs. Initial simulations indicate that the analysis can extract meaningful data when the S_a/N << 1 (~ 0.1). This could lead to detection of some of the HAPs at threshold concentrations of ppb. This is achievable because all the wavelengths in the broad spectrum contribute to identifying the various features (strength and shape) of the absorption band. Averaging of the signal and training of the optimization algorithm using multiple shots (ten's to hundred's) are also factors in improving the prediction accuracy of the program over the background noise. With a high repetition rate UB radiation source, data collection will still be finished in matter of seconds. The computer

program is run on a desktop PC. It is possible to streamline the software to allow for automation of the data collection and analysis tasks.

The limiting S/N ratio in the detection system described above depends on the electronic noise of the detector. The noise from the background sunlight is a systematic contribution. One could increase the detector gate time to increase the volume of HAPs to be tested and hence lower the threshold HAP concentrations estimated above. The downside of this is that more of the background sunlight will be admitted to the detector. However, this would for the most part only raise the base level of the detector signal and reduce its dynamic range without hurting the S_a/N too much..

The analysis performed in the previous section has the same basic arguments used in our original proposal to the SERDP. The calculations are more refined and more details are shown. Many inputs to the analysis come from knowledge we have accumulated during the last years of research supported by SERDP. We have now generated UB radiation consistently using several approaches. We have a known bandwidth for the UB radiation that we can identify HAPs with absorption bands that fall within it. We have knowledge of the energy per pulse that we can generate and we are now working on increasing the repetition rate. We have developed a Kalman filter based signal processing program to analysis the absorption data that promises data reduction at S_a/N < 1.

A fundamental area that require further research is to extend the bandwidth of the UB radiation source to longer wavelengths where there are stronger and better documented absorption structures for many HAPs. In table I, the 4.609 μm absorption line of CO is included as an illustration of how a fundamental (as opposed to an overtone at 1.564 μm) absorption line can affect the detection threshold of a HAP. Extending the spectral width of the UB radiation requires novel techniques using different nonlinear material and/or a different laser source for the UB generation. We have identified a line of attack on this problem and will continue to investigate it as a long term goal.

In order to utilize the present UB radiation for practical remote sensing applications, the following areas need to be improved.

- A) To mitigate the signal to noise problem, the best solution is to increase the signal. We are generating ~ 1 mJ per pulse of UB radiation. This energy

limitation primarily arises from the amount of power one can send down an optical fiber because we are operating very close to the breakdown threshold power of the fibers. One can improve the situation by using laser pulses with longer pulse lengths. We are presently operating at 300 psec and are working on new lasers that can produce the same power with longer pulses and higher energy per pulse. Other engineering solutions are under consideration such as multiplexing the laser output to couple to multiple fibers at the expense of increasing the source size and degrading the propagation characteristics of the UB radiation.

- B) A high repetition rate of 1 kHz is technically feasible but this is again another engineering problem that a CRADA partner could do.
- C) The fast gating for the detector is an issue for ranging application of the UB remote sensing. Infrared detector technology has not reached the matured stage of incorporating gated image intensifiers like the visible to near infrared silicon detectors. External gating mechanisms have to be provided. Electronic gating is usually limited to μ sec timing for the gate window. Novel optical gating schemes are needed for sub-microsecond window timing and they are being considered at NRL. However, until we have confidently established experimentally the capability of the UB radiation to perform HAP absorption spectroscopy, we shall postpone investigation of this problem.
- D) To obtain reliable absorption spectra from the HAPs and analyze them for concentrations requires continued development of the software programs and implementation of the appropriate hardware. We shall concentrate on a HAP with large cross section such as acetylene to benchmark and to smooth out the hardware integration in the detector system.
- E) The question of whether to use a two dimensional array or two linear arrays to record the outgoing source spectrum and the incoming absorption spectrum is being considered. Because of the high frequency nature of our UB radiation pulses (300 psec), there are problems with the 2D array (both speed and sensitivity) that render its versatility in 2D imaging less attractive. Two linear

arrays may not be as convenient to use but they do offer the appropriate speed and sensitivity for our experiment.

V. Acknowledgements

This work is supported by the Strategic Environmental Research and Development Program and the Office of Naval Research.

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